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## SPECIFICS OF THE FORMATION OF A TRANSPARENT GLAZE LAYER ON CERAMIC FACING TILES

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The effect of modifiers of the  $\text{Na}_2\text{O}(\text{K}_2\text{O}) - \text{B}_2\text{O}_3 - \text{Al}_2\text{O}_3 - \text{SiO}_2$  glass-forming system on the nature of phase separation is studied. Certain regularities for the formation of a transparent glaze layer under accelerated firing conditions are established.

The formation of a transparent glaze layer on ceramic facing tiles at decreased temperatures and accelerated firing regime is a relatively complicated problem involving materials and technology. The known compositions of transparent glazes are either obtained in the multi-boron region of the  $\text{R}_2\text{O} - \text{RO} - \text{B}_2\text{O}_3 - \text{Al}_2\text{O}_3 - \text{SiO}_2$  system with a  $\text{B}_2\text{O}_3$  content of 25–35% (here and elsewhere molar content is indicated) or require protracted holding at firing temperatures around 1000°C [1, 2].

However, the need for developing competitive products stimulates research into contemporary decoration techniques for ceramic construction materials, which include the use of transparent glazes.

The technological problem of formation of a transparent glaze layer consists in the need to control the delicate phase separation processes which have a determining role in securing visual transparency in the glaze layer. It determines the development of the glaze composition allowing for the formation of a high-quality glaze coating at relatively low temperatures (about 900°C) under accelerated firing conditions, when the second firing cycle does not exceed 50 min.

The formation of a single-phase vitreous coating is optimum as far as transparency is concerned. However, this is hard to achieve, since virtually all technologically suitable glass-forming systems which can be used to obtain glaze coatings have ample liquation areas. Repeated heat treatment of powdered vitreous materials within the temperature range of metastable liquation facilitates the development of the liquation processes, which determines the opacification of the glaze layer. Therefore, in the synthesis of transparent glazes, we did not strive to develop a single-phase vitreous structure for glaze coating. It was desirable to decrease the propensity to phase separation, which should be expressed in

a decrease in the size of liquation-type inhomogeneities and the volume of the drop phase.

According to the authors of [2], the transparency of a glaze layer can be ensured by the development of a liquation structure with drop size 0.05–0.20 μm. Therefore, in designing the experimental compositions for transparent glazes we proceeded from the need for introducing components which have a homogenizing effect due to the decrease in the metastable liquation temperature and reduction of the liquation area.

The basis for the development of transparent glazes was the high-siliceous region of the  $\text{Na}_2\text{O}(\text{K}_2\text{O}) - \text{B}_2\text{O}_3 - \text{Al}_2\text{O}_3 - \text{SiO}_2$  system. The content of boron oxide in the synthesized glass did not exceed 20%. The homogenizing role of aluminum oxide is well known; however, its content in the experimental compositions was limited to 5%, which was due to the technology requirements: the glass-melting temperature should be 1400 ± 20°C; for satisfactory spread of the glaze layer, the maximum temperature of the second firing should be 920 ± 20°C. In order to improve the technological properties, modifying oxides (CaO, SrO, BaO, PbO) were added to the compositions.

The ceramic base consisted of a multicomponent mixture whose crack water absorption after the first firing was 18–20% and whose TCLE was  $(73 - 76) \times 10^{-7} \text{ } ^\circ\text{C}^{-1}$ .

The study of the technological properties of the modified glasses and coatings based on them revealed that the oxides of bivalent metals with respect to their intensifying effect on the opacification of coatings are positioned in the CaO, BaO, PbO series. The effect of SrO is comparable to that of CaO, but the latter component is preferable, since it is introduced with a less expensive raw material. It should be noted that the nature of the effect of lead oxide on the quality of glaze coating significantly depends on its content: if its quantity does not exceed 15%, transparency and fine spread are not provided. With further increase in the PbO content, a transparent

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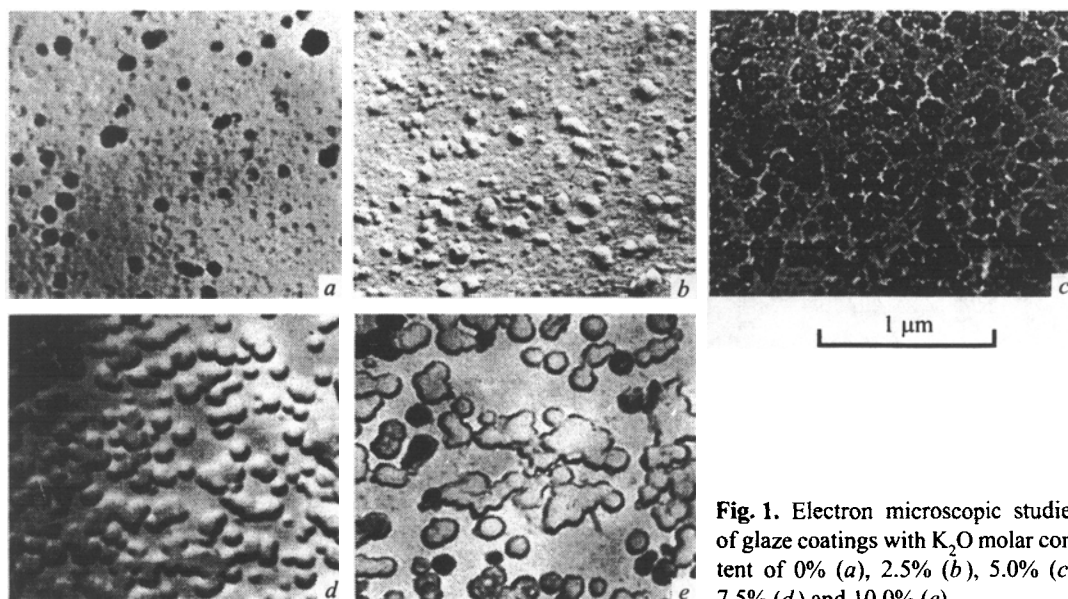


Fig. 1. Electron microscopic studies of glaze coatings with  $K_2O$  molar content of 0% (a), 2.5% (b), 5.0% (c), 7.5% (d) and 10.0% (e).

glaze coating with fine spread and luster is formed. However, lead-bearing glazes are not suitable for the decoration of facing tiles, since they do not satisfy the required heat resistance level. The ambiguity of the lead oxide effect is related to the structural specifics of lead-containing glasses [3].

The content of calcium oxide in glass compositions used for transparent glazes is limited to 5–8%, since its increase intensifies the opacification of the coatings formed. This is determined by the development of liquation processes, and when the  $CaO$  content is above 15%, by the crystallization processes as well.

For the purpose of improving the technological properties of glazes,  $K_2O$  equimolarly substituted for  $Na_2O$ , with a constant total content of alkaline oxides equal to 10%, is recommended. The amount of introduced  $K_2O$  varied from 0% to 10% with a 2.5% step. The results obtained in fusing of potassium-bearing coatings were as follows: with an increase in the content of  $K_2O$  at the expense of  $Na_2O$ , the degree of opacification of the coating increases. Electron microscopic studies revealed that sodium-containing coatings have a heterogeneous liquation-type structure with a drop size not more than  $0.1 \mu m$  (Fig. 1). When  $Na_2O$  is replaced by  $K_2O$  and the content of the latter increases, the drop size and the number of drops per unit of volume increase until they merge and form a double-skeleton liquation structure.

According to the data on the liquation areas in the  $R_2O - B_2O_3 - SiO_2$  ternary systems summarized in [4], the tendency to phase separation in alkali-boron-silicate systems in the  $Li_2O$ ,  $Na_2O$ ,  $K_2O$ ,  $Rb_2O$ ,  $Cs_2O$  series continuously decreases, and with an increase in the alkali ion size, the liquation regions become narrower.

Since the results obtained cannot be uniquely explained from the point of view of the known concept of the effect of alkaline oxide on the phase separation process, additional in-

vestigations of potassium-containing glaze glasses were carried out.

Gradient heat treatment of the glasses within a temperature range of 500–1000°C for 1 h indicated that with an increase in the content of  $K_2O$ , the degree of opalescence in the glass increases up to its opacification, and the boundary of the visually transparent glass is shifted toward the higher temperatures. The most significant increase in the maximum temperature at which opacification of samples was registered, was typical of glasses whose  $K_2O:Al_2O_3$  ratio exceeded 1. Thus, the opalescence temperature interval in glasses containing 7.5–10.0%  $K_2O$  ranges from 650 to 920°C. Moreover, in the case of complete replacement of sodium oxide in the glass composition with an equimolar quantity of potassium oxide, the initial glass samples produced by casting had rainbow opalescence. Accordingly, the glaze coatings based on glasses with a predominant content of potassium oxide were opacified, and the degree of opacification increased with increase in the  $K_2O$  content. It should be noted that the opacified glasses are x-ray amorphous, i.e., the opacification of glasses and coatings is related to the emergence of liquation processes, which is supported by the data of electron microscopic studies.

This unusual effect of potassium oxide on the phase separation processes is manifested only in multicomponent oxides which contain, beside the alkaline oxides, also an oxide of the RO group as a modifier; in the given case it is  $CaO$ . In the absence of  $CaO$ , the glasses treated according to the specified procedure are visually transparent. The content of  $B_2O_3$  also has an effect on the technological properties of experimental glasses: its decrease eliminates the opacification and opalescence of the treated samples.

Another effect of potassium oxide which is unusual from the traditional point of view was reported by the authors of [5] who investigated the liquation processes in glasses of the

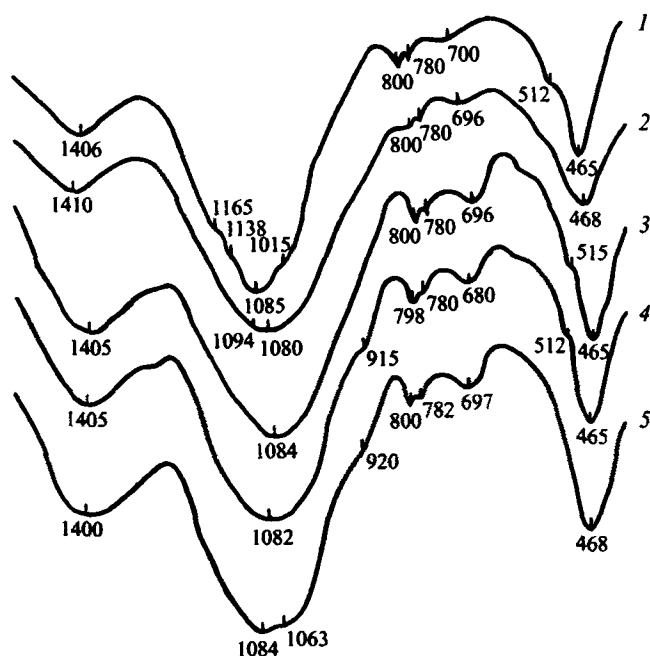


Fig. 2. IR spectra of glaze glasses with molar content of  $K_2O$ : 0% (1), 2.5% (2), 5.0% (3), 7.5% (4) and 10.0% (5).

$R_2O - CaO - Al_2O_3 - SiO_2$  system: simultaneous addition of  $Na_2O$  and  $Al_2O_3$  in equimolar quantities to liquating calcium-silicate glasses results in their homogenization, while on the introduction of  $K_2O$  and  $Al_2O_3$ , a substantial liquation is observed. The authors attribute this phenomenon to a variation in the distribution coefficient of the tetrahedral aluminate complexes  $[AlO_{4/2}]Na$  and  $[AlO_{4/2}]K$  between the coexisting vitreous phases: sodium aluminate mostly in the high-cation phase and potassium aluminate in the highly siliceous phase.

Aluminum oxide has a homogenizing role in the investigated glasses. This role is probably related not only to the formation of alkaline-aluminate complexes and their incorporation in the silicon-oxygen skeleton, but also to the effect of  $Al_2O_3$  on the kinetics of liquation separation, due to an increase in the low-temperature and high-temperature viscosity, which is especially significant in the case of short-term heat treatment.

Identification of the structural groups in aluminoborosilicate glasses based on IR-spectrometry data is difficult, owing to the superposition of the absorption bands corresponding to the atom vibrations in the  $Si^{IV} - O - Si^{IV}$  and  $B^{IV} - O - B^{IV}$ ,  $B^{III} - O - B^{III}$  and  $B^{III} - O - B^{IV}$ ,  $Al^{IV} - O$  [6, 7] bonds. However, the no less obvious variation in the IR absorption spectrum on replacement of  $Na_2O$  with  $K_2O$  in glasses with a constant content of glass-forming oxides (spectra 1 and 5 in Fig. 2) gives ground for certain conclusions concerning the effect of this substitution on the coordination state of the elements which are active in a given spectral range.

The distinctive features of the potassium-containing glass spectrum is an increase in the intensity of the absorption bands with maxima at 1400 and 700  $cm^{-1}$ , a clear expression of an arm at 920  $cm^{-1}$ , and a wide absorption band of 1200–900  $cm^{-1}$  typical of silicate glasses. These variations in the absorption spectra are evident on equimolar replacement of  $Na_2O$  with  $K_2O$  (spectra 2–4 in Fig. 2). Since the content of  $CaO$  and  $Na_2O(K_2O)$  in the analyzed glasses exceeds significantly the content of  $Al_2O_3$ , it can be assumed that aluminum is related to tetrahedral coordination, and the contribution of groups  $[AlO_{4/2}]^-$  to the characteristic absorption bands (720–780  $cm^{-1}$ ) is a constant value.

According to the data in [6], the absorption maximum at 920–970  $cm^{-1}$  in borate glasses relates to the valence asymmetric atom vibrations in the bonds  $B^{IV} - O - B^{IV}$ . The intensification of absorption bands with maxima at 1400 and 700  $cm^{-1}$  is probably determined by the increase in the number of atoms with  $B^{III} - O - B^{IV}$  bonds. Hence it follows that the substitution of  $K_2O$  for  $Na_2O$  in the composition of the analyzed glasses produces an increase in the fraction of  $[BO_{4/2}]^-$  structural groups. It should be noted that the absorption band at 920  $cm^{-1}$  in silicate glasses is often associated with the phenomenon of atom vibrations in the  $Si^{IV} - O^-$  bonds. The modifying ions in the analyzed highly siliceous glasses are mainly included in the aluminate and borate structural groups whose stability increases in the  $Ca^{2+} - Na^+ - K^+$  series; therefore, the prerequisites for an increase in the fraction of the  $Si^{IV} - O^-$  nonbridging bonds are absent.

Thus, according to the data of the IR spectroscopy, the structure of potassium-containing glasses is characterized by a larger fraction of the four-coordination boron due to the formation of  $[BO_{4/2}]K$  complexes which are more stable than the  $[BO_{4/2}]Na$  complexes, owing to the lower electronegativity of the  $K^+$  ion. An increase in the amount of structural groups with the  $B^{III} - O - B^{IV}$  bonds is probably due to the fact that  $K_2O$  mostly dissolves in the boron-enriched phase.

The author of [8, 9], investigating the phase separation in sodium-borosilicate glass, suggested that the increase in liquation temperature and the rate of nucleation of liquation inhomogeneity areas caused by introduction of  $V_2O_5$  and  $CaO$  additives is determined by their surface activity in silicate melts.

With respect to the surface activity and the effect on the surface tension at the boundary between the liquating phases, the  $Na_2O$  and  $K_2O$  components are not equivalent. According to the classification in [10],  $Na_2O$  belongs to oxides which are surface-inactive in silicate melts, and  $K_2O$  belongs to the group of intermediate oxides which are characterized by low partial values of surface tension. The decrease in the surface tension and low-temperature viscosity, which occurs on introduction of  $K_2O$ , apparently, increases the rate of nucleation of liquation inhomogeneity areas, which is reflected in the increased amount of liquation drops.

The complexity of the chemical composition of the analyzed glasses related to the  $\text{Na}_2\text{O} - \text{K}_2\text{O} - \text{CaO} - \text{B}_2\text{O}_3 - \text{Al}_2\text{O}_3 - \text{SiO}_2$  system hampers the structural interpretation of the effect of individual oxides on the liquation process. It can be assumed that the evolution of the liquation processes with simultaneous introduction of such modifiers as  $\text{K}_2\text{O}$  and  $\text{CaO}$  to the boron-containing glass is related to the variation in the composition of the coexisting phases and the phase separation kinetics.

Conditions for the nucleation of micro-inhomogeneity areas of the liquation type in potassium-containing glasses develop upon repeated heat treatment of glaze coatings. In this case, the degree of dispersion of the drop liquation structure of the glaze layer to a great extent depends on the cooling rate: with decrease in the cooling rate, the drop size increases, which causes partial opacification and a decrease in the coating luster. In this case, the use of an accelerated firing procedure is a positive technological factor.

The technological specifics of transparent glazes include a need for careful selection of milling additives. The particles of refractory white-burning clay added in milling of the opacified glaze frit determine the development of phase separation processes in the glaze layer and, consequently, the deterioration of glaze transparency and luster. Therefore, the required rheological properties of glaze slip and the strength of adhesion of raw glaze layer are provided mainly by the introduction of increased quantities of polymers soluble in water.

As a result of our experiments, a transparent glaze for facing ceramics was developed, which contains less than 20 mole % boron oxide and is fired according to an accelerated procedure (firing cycle 40 min) at a maximum tempera-

ture of  $900 \pm 20^\circ\text{C}$ . The obtained ceramics are characterized by good luster (70 – 75 by an FB-2 luster meter), increased hardness (at least 8 on the Mohs scale), and sufficient heat stability.

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